Coexistence of Antiferromagnetism and Superconductivity in $PrFeAsO_{1-\delta}$

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Abstract

A high-quality $PrFeAsO_{1-\delta}$ single crystal (T_c = 44 K) has been investigated by the magnetic torque. Antiferromagnetism of the Pr^{3+} ions was found to coexist with superconductivity in $PrFeAsO_{1-\delta}$ at temperatures below $T_N = 14$ K. We predict a magnetic structure that is not in accordance with earlier neutron studies performed using polycrystalline nonsuperconducting specimens. As the temperature decreases, the superconducting anisotropy $\gamma \sim 4$ of $PrFeAsO_{1-\delta}$ increases near T_c and tends to decrease slightly at lower temperatures.

Keywords: $PrFeAsO_{1-\delta}$, single crystal, torque, anisotropy, antiferromagnetism, weak ferromagnetism

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Since the discovery of superconductivity in the iron oxypnictide $LaFeAsO_{1-\delta}F_{\delta}$ [1] considerable effort has been made to understand the superconducting mechanism of this and similar materials. Other iron oxypnictides have subsequently been reported to show T_c as high as 55 K and several promising applications in various fields using these materials have been identified. The superconductivity in iron-oxypnictides has a rich variety of derivatives, i.e., the so-called 1111 phase [2, 3], the 122 phase [4], the 111 phase [5], and the 11 phase [6, 7].

Achieving a high superconducting T_c is a goal of contemporary scientific research. An interesting finding is that antiferromagnetism is often closely tied with possible high-T_c. For instance, the high-T_c cuprate $HgBa_2Ca_4Cu_5O_y$ has five CuO_2 planes in a unit cell and its anisotropy ranges from 40 to 50 depending on the doping level [8]. ^{63,65}Cu-NMR measurements of $HgBa_2Ca_4Cu_5O_y$ have revealed that disparate electronic phases emerge at the outer two superconducting CuO_2 planes and the inner three antiferromagnetic layers; the outer plane undergoes a bulk superconducting transition at $T_c = 108\,\mathrm{K}$ and the underdoped inner plane shows a antiferromagnetic transition below $T_{\mathrm{N}} = 60\,\mathrm{K}$ [9].

It is of great importance to determine whether magnetism and superconductivity can coexist in iron arsenic superconductors. For example, a transition from a paramagnetic state to an antiferromagnetic state has been reported for both Fe^{2+} and Pr^{3+} ions. However, this is only the case for undoped non-superconducting samples [10]. Superconducting samples do not show antiferromagnetism. McGuire *et al.* [11] studied Mössbauer spectroscopy of RE1111 samples (RE = La, Ce, Pr, Nd) and did not find any evidence for antiferromagnetism in La1111 and Nd1111, while they found T_{N} = 3.8 K for Ce1111 and T_{N} = 13 K for $PrFeAsO_{1-\delta}$. Note that their studies were carried out using undoped specimens.

Zhao *et al.* [12] have reported systematic studies of $CeFeAsO_{1-x}F_x$ as a function of doping x, and confirmed three independent phase transitions, i.e., structural phase transition, antiferromagnetic transition of Fe spins, and antiferromagnetic transition of Ce spins. To the authors' knowledge, the magnetic ordering in RE1111 systems has been reported only for undoped nonsuperconducting systems, by neutron diffraction [10, 12, 13], Mössbauer spectroscopy [11], and μSR spectroscopy [14, 15]. Neutron studies of magnetic ordering in RE1111 systems suggest that Fe^{2+} spins are in an antiferromagnetic state along the a axis while Pr^{3+} spins are in an antiferromagnetic state along the c axis [10]. Superconductivity only appears in a regime where antiferromagnetism disappears as a function of x.These find-

ings strongly suggest that it is very hard for iron arsenic superconductors to accommodate antiferromagnetism and superconductivity simultaneously.

In contrast to this result, recent ^{149}Sm nuclear resonant forward scattering (NRFS) measurements by Kamihara *et al.* [16] indicate that an antiferromagnetic Sm sublattice appears in the superconducting phase of $\mathrm{SmFeAsO}_{1-x}\mathrm{F}_x$ ($x = 0.069$) below $T_\mathrm{N} = 4.4\,\mathrm{K}$ while the undoped sample has $T_\mathrm{N} = 5.6\,\mathrm{K}$. Magnetism from Sm^{3+} ions has also been reported in the optimal superconducting phase in $\mathrm{SmFeAsO}_{1-x}\mathrm{F}_x$ ($x = 0.15$) [17]. Drew *et al.* [18] have reported antiferromagnetic ordering of Sm spins below 5 K by means of ZF-μSR measurements as well as specific heat measurements for $\mathrm{SmFeAsO}_{1-x}\mathrm{F}_x$ ($x = 0 - 0.2$). However, no magnetic orderings have been observed so far for superconducting $\mathrm{PrFeAsO}_{1-x}\mathrm{F}_x$ [19]. We argue that it is necessary to carry out further studies on the possible coexistence of superconductivity and antiferromagnetism using high-quality crystals of iron arsenic superconductors.

The magnetic torque is a good measure of electronic anisotropy, including magnetism and superconductivity. In this Letter, we report clear evidence for the coexistence of antiferromagnetism and superconductivity from systematic measurements of the magnetic torque of a high-quality superconducting $\mathrm{PrFeAsO}_{1-\delta}$ single crystal.

The $\mathrm{PrFeAsO}_{1-\delta}$ single crystal had a plate-like shape ($560\times400\,\mu$m in size, $19\,\mu$m in thickness), of which the critical temperature T_c was determined to be 44 K by a SQUID magnetometer. The torque is a bulk probe and is defined as the angular derivative of the free energy F with respect to θ, $\tau(\theta) = -\partial F/\partial\theta$. The reversible torque is evaluated as $\tau_\mathrm{rev}(\theta_c) = (\tau_\mathrm{inc}(\theta_c) + \tau_\mathrm{dec}(\theta_c))/2$, where $\tau_\mathrm{inc}(\theta_c)$ and $\tau_\mathrm{dec}(\theta_c)$ represent the torque as functions of increasing and decreasing θ_c, respectively. θ_c is the angle between the applied magnetic field H and the c-axis. The anisotropic paramagnetism gives a torque expressed by $\tau_\mathrm{pm}(\theta_c) = \frac{1}{2}(\chi_a - \chi_c)H^2V\sin 2\theta_c = \Delta\tau_\mathrm{pm}\sin 2\theta_c$ where χ_a and χ_c are the susceptibility along the a-axis and that along the c-axis, respectively. The paramagnetic anisotropy in $\mathrm{PrFeAsO}_{1-\delta}$ is presumably due to Pr^{3+} spins. In Fig. 1, the coefficient $\Delta\tau_\mathrm{pm}$ of $\sin 2\theta_c$ is plotted as a function of T by analyzing the $\mathrm{PrFeAsO}_{1-\delta}$ torque curves in a magnetic field of 30 kG. The data is fitted to the Curie–Weiss law of Pr^{3+} spins in the normal state from 47.5 to 180 K.

The $\sin 2\theta$ component consists of the anisotropic paramagnetism $\Delta\tau_\mathrm{pm}$, the *effective* excess contribution $\Delta\tau_\mathrm{sc}$ due to superconductivity, and the antiferromagnetism $\Delta\tau_\mathrm{AF}$ (see the inset of Fig. 1). We find that the enhanced coefficient of sin 2θ, in excess of that predicted by the

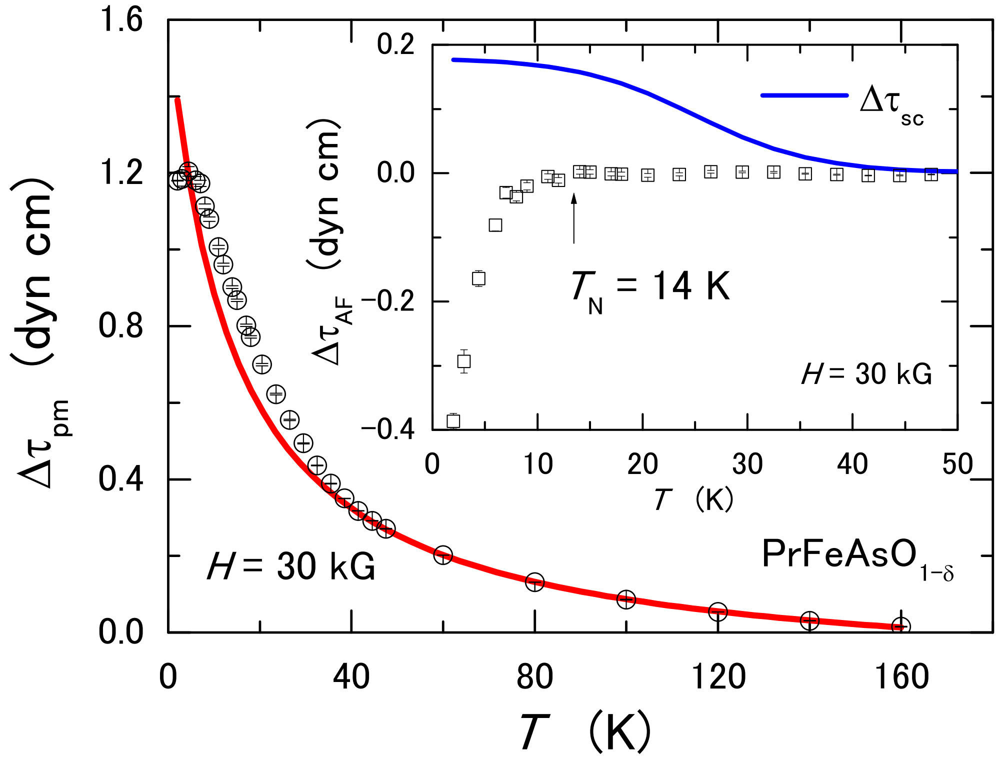

FIG. 1: (Color online) The $\sin 2\theta$ component of the $PrFeAsO_{1-\delta}$ torque as a function of T in a magnetic field of 30 kG. The solid line represents the least-squares fit to the Curie–Weiss law $\tau_{2\theta} = C/(T-\Theta)+\tau_0$ ($C = 24.4 \pm 2.1$, $\Theta = 14.1 \pm 3.8$ K, $\tau_0 = -0.13 \pm 0.01$) in the normal state. After subtracting the superconducting torque $\Delta\tau_{sc}$ of the inset (see text), the torque followed the curve $\Delta\tau_{AF}$, demonstrating clear evidence for antiferromagnetism at temperatures below 14 K.

Curie–Weiss law, is due to anisotropic superconductivity in $PrFeAsO_{1-\delta}$. For simplicity, the superconducting torque was approximated by a presumed line $\Delta\tau_{sc} = \Delta\tau^0_{sc}[1-\tanh(T-T_{mid})/T_{width}]$ ($\Delta\tau^0_{sc} = 0.09 \pm 0.002$ dyncm, $T_{mid} = 25.1 \pm 0.44$ K, $T_{width} = 11.3 \pm 0.5$ K), saturated at low temperatures. Antiferromagnetism appears at temperatures below 14 K after subtracting the superconducting torque $\Delta\tau_{sc}$. Our torque measurements show that the susceptibility follows the relation $\chi_a > \chi_c$ even at temperatures below T_N. This strongly indicates that the c axis should be considered the easy axis of the antiferromagnetic state in $PrFeAsO_{1-\delta}$. We argue that the spin configuration in the antiferromagnetic state is inconsistent with the findings of neutron diffraction experiments on a non-superconducting polycrystalline sample [10]. The sign of $\Delta\tau_{2\theta}$ in the torque curve remains unchanged in both the normal and superconducting states. Therefore, the direction of the antiferromagnetic

spins should be parallel to the *ab* plane. In view of the fact that the antiferromagnetic torque $\Delta\tau_{\mathrm{AF}}$ is appreciable compared to the superconducting torque $\Delta\tau_{\mathrm{sc}}$ (see inset of Fig. 1), the antiferromagnetism at temperatures below T_c cannot be explained by an impurity phase.

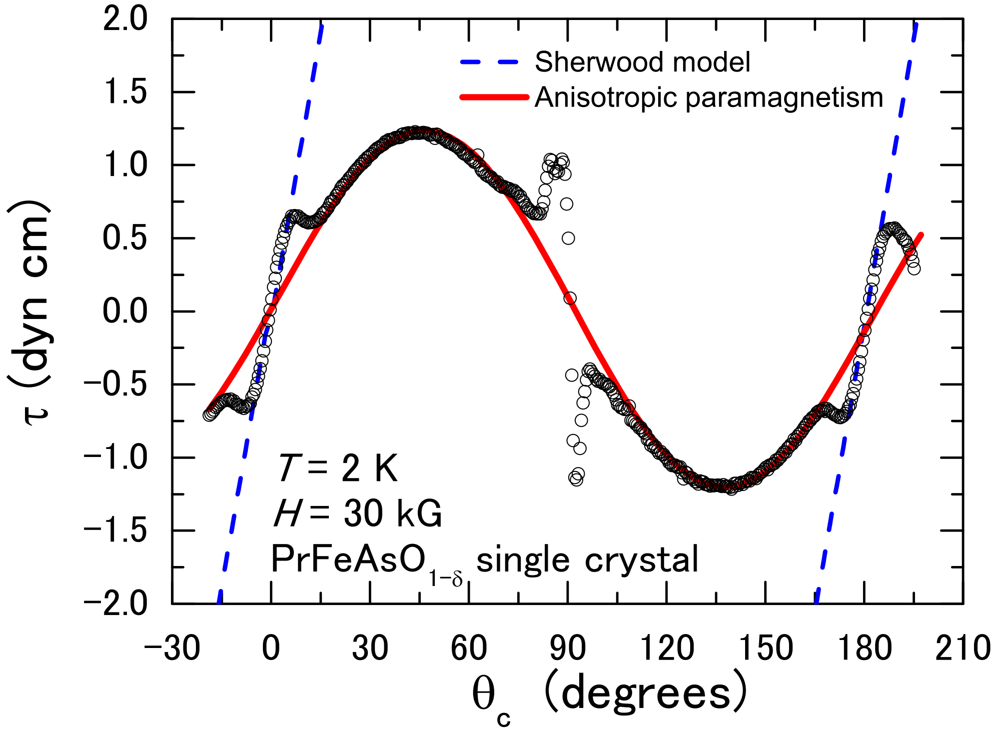

FIG. 2: (Color online) The reversible torque curve (open circles) in 30 kG and at 2 K. The solid line shows a fit to $\tau(\theta_c) = \Delta\tau \sin 2\theta_c$ ($\Delta\tau = 1.18 \pm 0.01$). The dashed line shows a fit to the Sherwood model $\tau_{\mathrm{wf}}(\theta_c) = \pm\sigma_0 HV \sin\theta_c$ ($\sigma_0 = 7.6 \pm 1.9$) of excess torque coming from field-induced weak ferromagnetism.

Fig. 2 shows the reversible torque of $PrFeAsO_{1-\delta}$ in 30 kG and at 2 K. In addition to the $\sin 2\theta$ component, we observe that the torque exhibits an unstable nature at $\theta_c = 0$. This unstable torque region appears only at temperatures lower than $T_{\mathrm{N}} = 14$ K, and its magnitude increases as T decreases. We argue that this unstable torque is due to weak ferromagnetism of $PrFeAsO_{1-\delta}$ induced in the antiferromagnetic ordered state when the field is applied parallel to the c axis. Sherwood *et al.* [20] proposed a torque model for field-induced weak ferromagnetism or parasitic magnetic ordering $REFeO_3$. The torque formula is given by $\tau_{\mathrm{wf}}(\theta_c) = \pm\sigma_\theta HV \sin\theta_c = \Delta\tau_\theta \sin\theta$, where the coefficient σ_0 is supposed to be independent of H and the sign ($\pm$) depends on the field direction in the crystal. Fig. 2 also shows a fitting curve of the enhanced unstable torque to $\tau_{\mathrm{wf}}(\theta_c) = \Delta\tau_\theta \sin\theta$. Note that the

formula becomes $\tau = \tau_{2\theta} \sin 2\theta$ for anisotropic paramagnetism. The magnetic contribution of Tm^{3+} in $TmFeO_3$ shows a similar anomalous torque curve when weak ferromagnetism is induced in the antiferromagnetic phase [21]. Field-induced canted ferromagnetism is a candidate to explain weak ferromagnetism yielding the $\sin\theta$ term in $PrFeAsO_{1-\delta}$ expected from the Sherwood formula [20]. Both anisotropic paramagnetism and antiferromagnetism yield the $\sin 2\theta_c$ term, arising from the difference in the susceptibilities along the *ab*-plane and the *c*-axis. It is worth noting that the sin 2θ term is proportional to H^2 while the $\sin\theta$ term due to spontaneous magnetization is proportional to H^1. We compared the prefactor τ_0 in 30 kG with that in 10 kG to investigate the origin of the anomalous magnetism. The ratio $\Delta\tau_{2\theta}(H = 30\,\text{kG})/\Delta\tau_{2\theta}(H = 10\,\text{kG})$ remains at 2.1 ± 0.3 while it is expected to reach 9. The ratio $\Delta\tau_{\theta}(H = 30\,\text{kG})/\Delta\tau_{\theta}(H = 10\,\text{kG})$ is 2.7 ± 0.5, in good accordance with the theoretical expectation of 3. We reasonably conclude that the origin of the singular torque curve for $PrFeAsO_{1-\delta}$ at $\theta_c = 0$ degrees is due to field-induced canted ferromagnetism.

Heat capacity measurements on $LaFeAsO_{1-x}F_x$ by Kohama *et al.* [22] suggest the occurrence of itinerant ferromagnetism. The appearance of ferromagnetic spin fluctuations in $LaFeAsO_{1-x}F_x$ is interpreted as being due to electronic interactions between itinerant quasiparticles. This anomaly indicates that ferromagnetic interaction between itinerant quasiparticles in the superconducting state in the Fe–As layers gives rise to a weak ferromagnetic state when an external field is applied to the system. A similar weak ferromagnetic spin fluctuation has been reported to occur in superconducting UCoGe [23]. The fact that ferromagnetic instability occurs in the vicinity of the superconducting state strongly suggests the occurrence of triplet superconductivity in UCoGe. It is not certain whether a similar scenario occurs in $PrFeAsO_{1-\delta}$, and further studies are needed.

The $PrFeAsO_{1-\delta}$ single crystal does not exhibit conventional intrinsic pinning above 14 K, while some high-T_c cuprates show an extremely sharp peak in the torque hysteresis at $\theta_c = 90$ degrees [24–27]. This is due to undulation of the order parameter perpendicular to the superconducting planes. The absence of conventional intrinsic pinning in the torque curve indicates modest anisotropy in oxypnictides. However, a novel intrinsic pinning behavior can be seen at temperatures below 14 K. As seen in Fig. 2, a steep stable point can be seen at $\theta_c = 90$ degrees of the torque curve. The torque hysteresis also shows a sharp peak at 90 degrees. This is very similar to the so-called intrinsic pinning that appears in various high-T_c cuprates [24–27]. We consider that this is due to the magnetic interaction between vortices

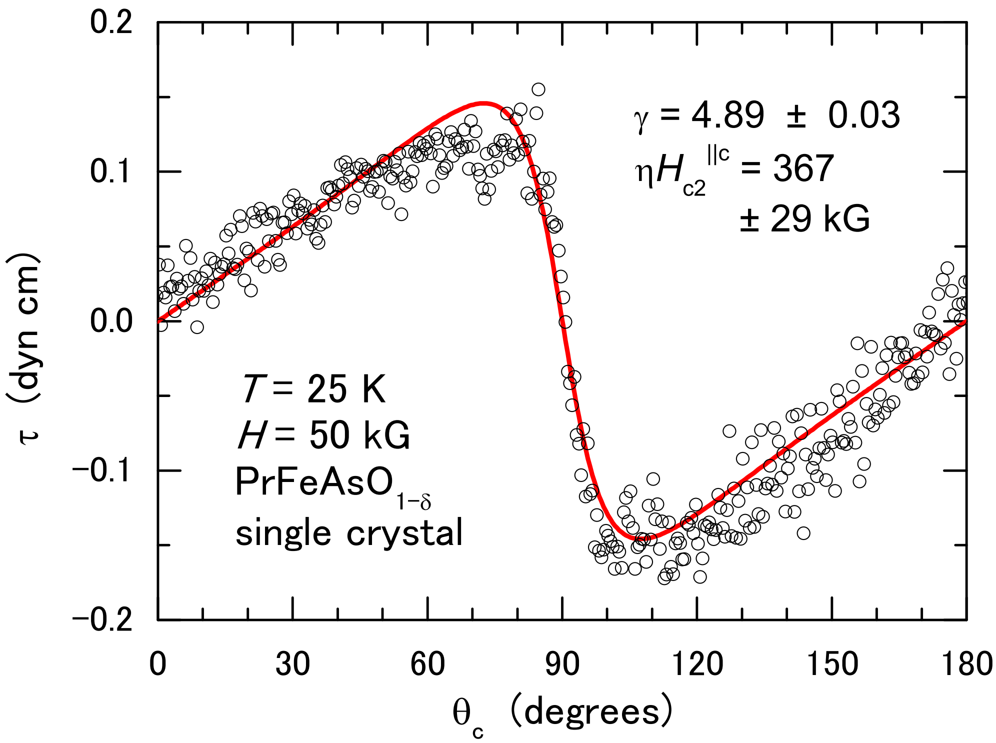

FIG. 3: (Color online) The reversible torque curve of the $PrFeAsO_{1-\delta}$ single crystal in 50 kG and at 25 K, where the paramagnetic contribution to the torque is subtracted. The solid line is the least-square fit to the Kogan model.

and antiferromagnetic spins. When the field is exactly parallel to the antiferromagnetic plane, the induced moment along the field may decrease the free energy compared to the paramagnetic case. This is also a sort of exotic intrinsic pinning, as first discovered by us at temperatures below T_{N}.

Conventional torque theory for anisotropic superconductors, developed by Kogan [28], is very useful for various types of superconductors [24–27, 29]. It is given by

$$\tau_{\mathrm{rev}}(\theta_c) \;=\; \frac{\Phi_0 HV}{16\pi\lambda^2}\frac{\gamma^2-1}{\gamma^{1/3}}\frac{\sin 2\theta_c}{\epsilon(\theta_c)}\ln\{\frac{\gamma\eta H_{c2}^{\|c}}{H\epsilon(\theta_c)}\} \tag{1}$$

where $\epsilon(\theta_c) = (\sin^2\theta_c + \gamma^2\cos^2\theta_c)^{1/2}$, $\gamma = \sqrt{m_c/m_{ab}}$, Φ_0 is a flux quantum, $H_{c2}^{\|c}$ is the upper critical field when the field is applied parallel to the c axis ($\eta \sim 1$), and V is the sample volume.

Fig. 3 shows a typical reversible superconducting torque curve of the $PrFeAsO_{1-\delta}$ crystal at 25 K and in 50 kG. The paramagnetic contribution to the $PrFeAsO_{1-\delta}$ torque curve was estimated in the regime between T_c and 180 K, and the superconducting torque was

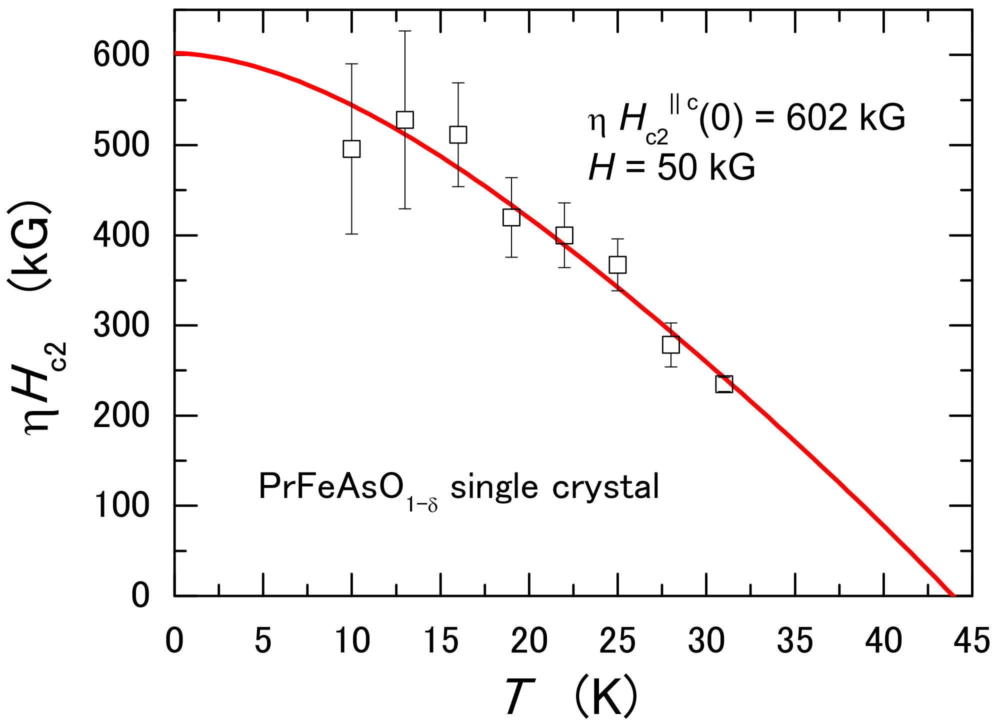

FIG. 4: (Color online) ηH_{c2} in 50 kG determined by the Kogan model as a function of T. The solid line is the least-square fit to WHH theory ($\alpha = 0$, $\lambda_{\rm SO} = 0$) [30].

extracted from the raw torque curve. The correction for antiferromagnetism is also taken into account. In the analysis of the torque curves in 50 kG, both γ and $\eta H_{c2}^{\parallel c}$ are treated as free parameters in the least-square fitting. In Fig. 4, $\eta H_{c2}^{\parallel c}$ as a function of temperature in 50 kG is approximated by a least-square fit to Werthamer–Helfand–Hohenberg (WHH) theory under the conditions $\alpha = 0$ and $\lambda_{\rm SO} = 0$ [30]. We predict $\eta H_{c2}^{\parallel c}(0) = 602\,{\rm kG}$ at $T = 0\,{\rm K}$ from the fitted curve. In Fig. 4, the solid line is a least-square fit curve by means of the single-band Kogan model with fixed ηH_{c2} of Eq. (1), where γ is the only fitting parameter and $\eta H_{c2}^{\parallel c}$ is taken from the solid line of Fig. 4.

We analyzed the torque using the Kogan model. In Fig. 5, we show the γ value of the PrFeAsO$_{1-\delta}$ single crystal compared with an undoped SmFeAsO$_{1-x}$F$_x$ single crystal ($T_{\rm c} = 45\,{\rm K}$) [31] as a function of temperature in 30 kG The γ value of PrFeAsO$_{1-\delta}$ increases slightly from 4 to 5 as T increases to 25 K while the γ of SmFeAsO$_{1-x}$F$_x$ varies from 4 to 11. The anisotropy of NdFeAsO$_{1-x}$F$_x$ single crystals ($T_{\rm c} = 51.5\,{\rm K}$) is also reported to increase from 4 to 6 ($5 < H < 90\,{\rm kG}$), determined from the angular dependence of the resistivity [32], γ of PrFeAsO$_{1-\delta}$ increases gradually from 4 to 4.7 between 4 K and 25 K, and then

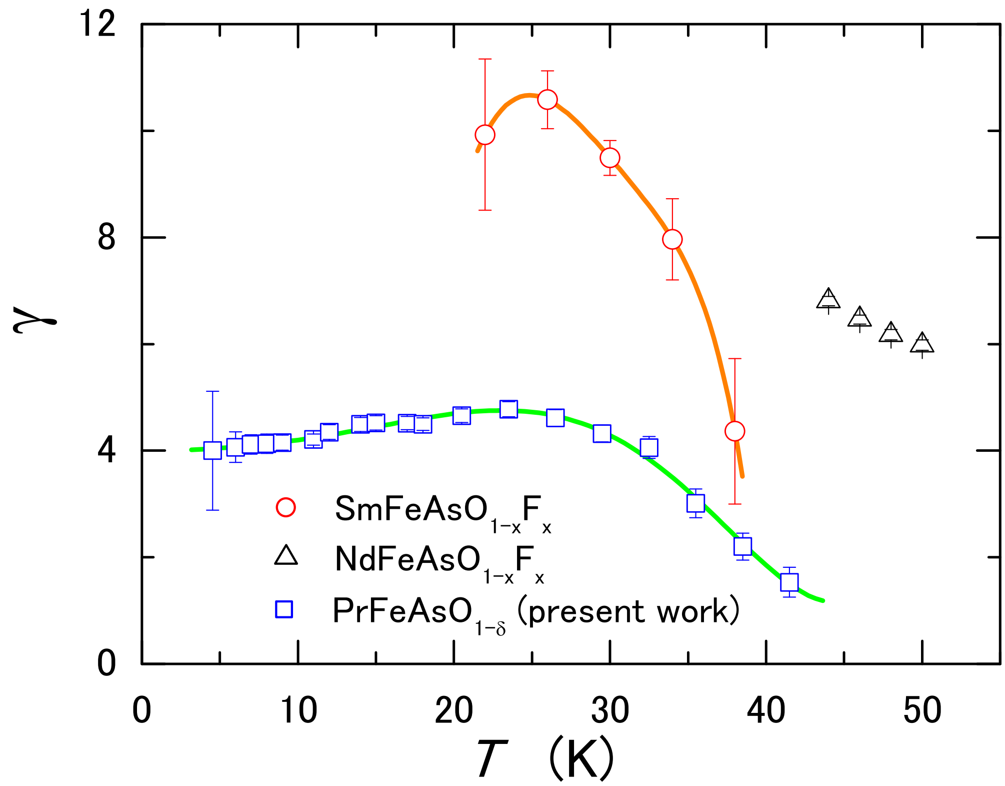

FIG. 5: (Color online) The anisotropy γ for $PrFeAsO_{1-\delta}$ determined in the present work (open squares). Data taken from $SmFeAsO_{1-x}F_x$ torque analysis in 30 kG (open circles) are also shown for comparison [31]. The anisotropy determined from the angular dependence of the resistivity of a $NdFeAsO_{1-x}F_x$ single crystal from 5 kG to 90 kG is also shown (open triangles) [32]. The lines are guides for the eye.

decreases down to 1.5 between 25 K and 41.5 K. $SmFeAsO_{1-x}F_x$ also exhibits a decrease in γ as T increases near T_c. A consideration of the effect of multiband superconductivity in $PrFeAsO_{1-\delta}$ [33] is of interest, and the theory for a multi-band superconductor has been reported [34, 35] and an improved theory will be published elsewhere [36].

In conclusion, the anisotropy parameter γ for $PrFeAsO_{1-\delta}$ is modest and changes gradually with temperature. After correcting the effect of the paramagnetic contribution on the torque curve, we can analyze the superconducting anisotropy γ using the Kogan model. A very interesting finding is that magnetic ordering at $T_{\mathrm{N}} = 14$ K appears even in the superconducting $PrFeAsO_{1-\delta}$ sample. This provides crucial evidence that superconductivity and antiferromagnetism can coexist at temperatures below T_{N} even in iron arsenic superconductors. Moreover, the appearance of field-induced weak ferromagnetism at temperatures below

T_N further confirms the appearance of antiferromagnetism.

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